Protein-like and humic fluorescence of CDOM in meromictic lakes of the White sea

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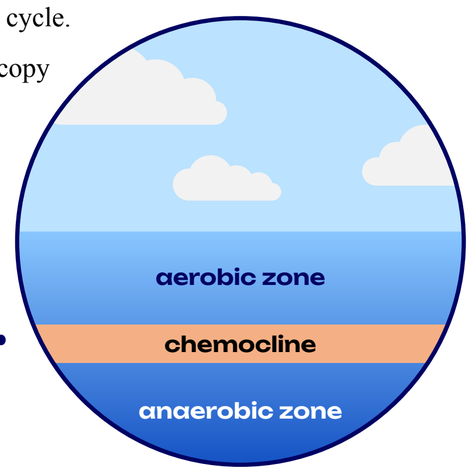
Relevance

Chromophoric dissolved organic matter (hereinafter CDOM) is a complex mixture that includes humic substances, proteins, amino acids, and their degradation products.
CDOM is a large reservoir of carbon, exceeding the reserves of all living organisms, which is why CDOM is of great importance for aquatic ecosystems and the global carbon cycle.

Since the quantitative and qualitative composition of CDOM significantly affects the optical properties of water, optical methods such as absorption and fluorescence spectroscopy are highly sensitive tools for non-destructive monitoring of CDOM and its transformation. Unique natural objects for such studies are meromictic water bodies, water bodies with stable vertical stratification, located at different stages of separation from the sea.



Objective of the research

This study is devoted to the investigation of the spectral-luminescent properties of CDOM in samples of natural water from meromictic water bodies of the White Sea: Lake Trekhtzvetnoe, a completely isolated water body, and the Biofilter Bay, which is at the initial stage of separation from the sea.

Materials and Methods

The study examined water samples from Lake Trekhtzvetnoe and the Biofilter Bay. Water samples were collected from various depths, covering the aerobic and anaerobic zones of the water bodies, as well as the chemocline (the zone of sharp changes in the chemical characteristics of the water).
In the chemocline zone, sampling was carried out at a more frequent interval.

The samples were filtered using syringe-type nylon filters with a pore size of 0.22 μm to remove suspended matter and microorganisms.

Spectrophotometry. Absorption spectra were recorded using a Solar PB2201 spectrophotometer in the range from 200 nm to 800 nm with a 1 nm step in quartz cuvettes with an optical path length of 2 cm. The optical density values are normalized to an optical path length of 1 cm.

Fluorimetry. The fluorescence emission spectra were recorded at different excitation wavelengths within the range from 250 nm to 500 nm, with a step of 10 nm, using a Solar CM2203 spectrofluorimeter for each depth.The spectra were recorded in the range from 260–515 to 700 nm.

For all measured fluorescence emission spectra, the effect of the internal filter was corrected using absorption spectra according to the formula:

$$I_{corr} = I_{meas} * 10^{\frac{D_{ex}+D_{em}}{2}}$$

where I_{corr} is the emission intensity corrected for the effect of the internal filter, I_{meas} is the measured emission intensity, D_{ex} and D_{em} are the optical density values of the sample at the excitation and emission wavelengths respectively.

Fluorescense Quantum Yield (FQY). The FQY is calculated using the reference dye method. Quinine sulfate was used as the reference; its quantum yield is: Φ = 0.55.
The calculation was carried out using the formula:

$$\Phi_{sample} = \Phi_{st} * \frac{K_{sample}}{K_{st}},$$

where Φ_{st} is the quantum yield of quinine sulfate, K_{sample} and K_{st} are the ratios of the integral fluorescence intensity across the spectrum to the optical density at the excitation wavelength for the water sample and the reference solution, respectively.

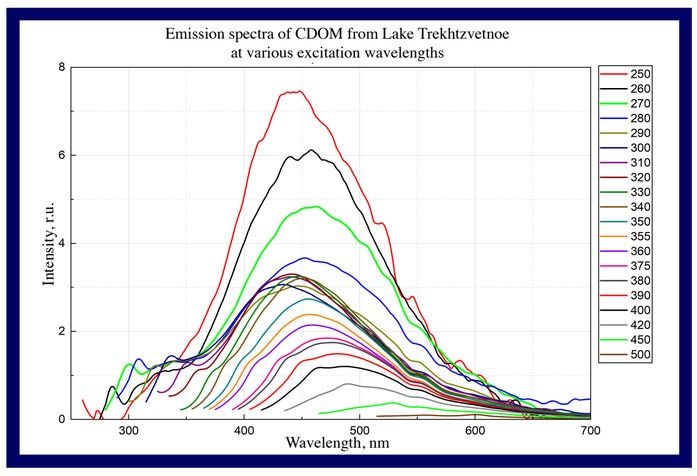
Results

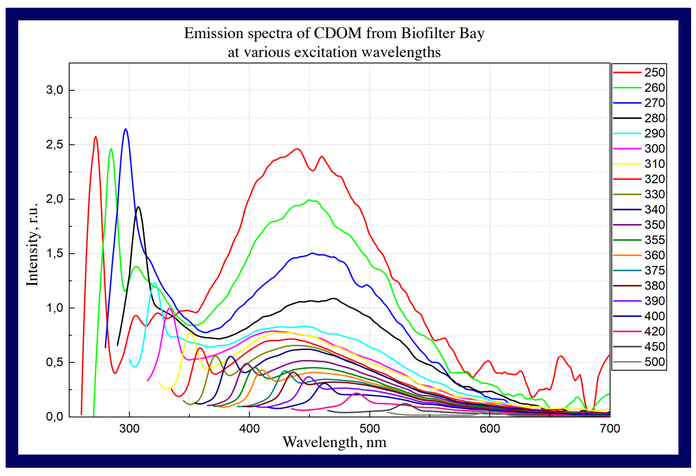
The obtained emission spectra for the two studied water bodies contain two fluorescence bands; the emission intensities and the ratios of these bands differ for the different water bodies. A signal from the Raman scattering (RS) of water is also visible as a peak that shifts to the long-wave region as the excitation wavelength increases.

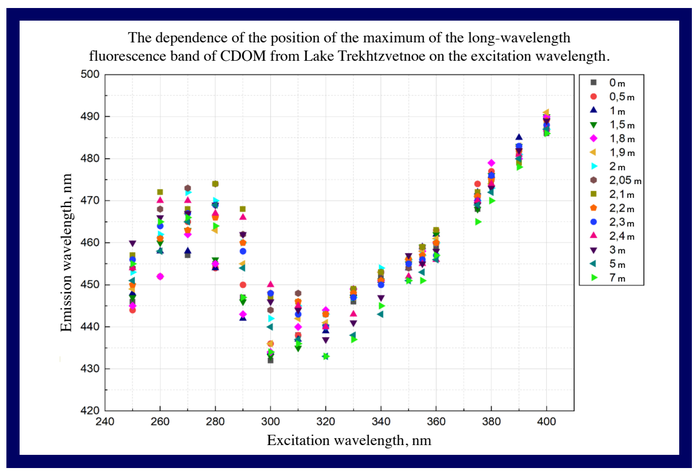
Based on the obtained fluorescence spectra, dependencies were constructed for the position and maximum value of the long-wavelength emission band of CDOM for two water bodies.

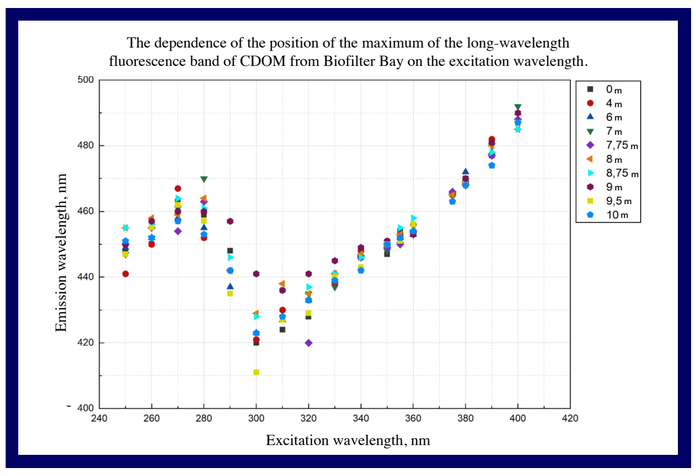
The constructed dependencies of the position of the emission maximum of the CDOM made it possible to estimate the magnitude of the “blue shift”, shift of the emission maximum to the short-wavelength region.

Using absorption and fluorescence spectra, the FQY for two reservoirs were calculated and the dependence of the FQY on the excitation wavelength was constructed.
Form of dependence of the FQY on the Lake Trekhtzvetnoe is the same for all depths, only the absolute values differ, which increase with depth. At the same time, the form of dependence for the Biofilter Bay is not so stable: there are no single maximum positions.





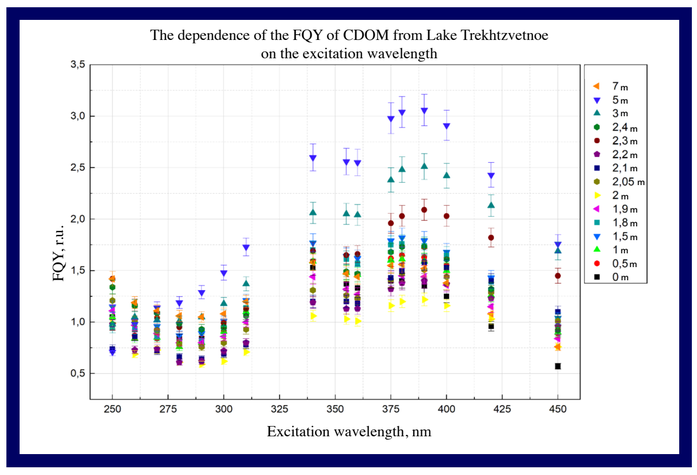


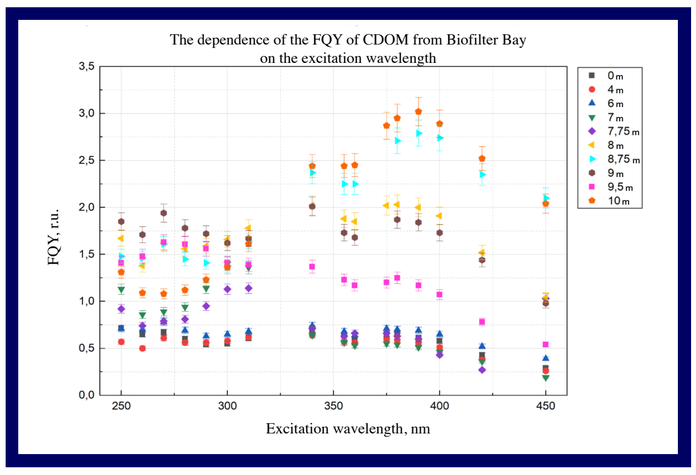


Conclusions

The analysis of the spectra revealed some important patterns:

1. In samples from the Lake Trekhtzvetnoe, completely isolated from the sea, ratio of the stripes was approximately constant at all depth horizons. At the same time, in the samples from Biofilter Bay it varied significantly with depth, which is probably due to the communication of surface waters with the sea. This allows us to draw an important conclusion that the ratio of bands depends on the composition of the CDOM, that varies depending on the stage of separation of the reservoir from the sea.
2. The calculation of the “blue shift” of the long-wavelength emission maximum for these water bodies showed that for the Biofilter Bay this value is higher than for Lake Trekhtzvetnoe, probably due to the greater contribution of fluorophores that emit in the short-wavelength region.
3. The dependencies of the FQY on the excitation wavelength showed different shapes for the two water bodies, which also reflects the differences in their CDOM composition.





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